

## SEAL Support

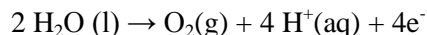
**This document describes the process of creating a template, how to deposit the mixed metal oxide combinations and prepare the samples for scanning.**

Participants of the Solar Hydrogen Activity Kit (SHArK)/Solar Energy Activity Laboratory (SEAL) project conduct research to find materials that are able to be used as a potential photoanode or photocathode of in a photoelectrochemical cell.<sup>1</sup> The SHArK/SEAL project tests two different deposition methods for the combinations of metal precursor solutions: pipetting and spraying. An overview of the experiment is as follows: select metal salt solutions as precursors, combine the precursors in varying ratios, deposit the precursors onto conductive glass plates, fire the plates for minimum of two hours to decompose the precursors into mixed metal oxides, test the combinations for photoactivity using one of the kits.

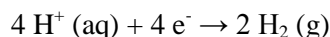
### The Basics

#### *Hydrogen Production*

Currently, hydrogen can be produced thorough the use of an electrolyzer which requires an external source of energy. The products are hydrogen and oxygen gas. The reaction takes place in an electrochemical cell known as an electrolytic cell, a cell that requires external energy to drive an otherwise thermodynamically non-spontaneous reaction. The cell contains an external source of energy, two electrodes, and an electrolyte. An amount of electrical energy is applied to an electrode. The change in voltage between the two electrodes in the electrolyte of the cell is the potential difference. At the surface of the electrodes, the supplied electrical energy is converted to chemical energy through charge exchange with the ions in the electrolyte.<sup>1</sup> An electrolyte is used instead of just water because water has a high resistivity and is a poor conductor. The solution can be an aqueous acid or alkaline material.<sup>1</sup> The two electrodes within the solution are responsible for the different half- reactions. One electrode is called the anode. The anode is the electrode where the oxidation of water occurs. The half-reaction for the oxidation is:



The cathode is the electrode where reduction of the hydrogen ions occurs. The half reaction for reduction is:



The drawback of the current electrolysis of water is the fact that energy must be supplied to drive the reaction of water splitting. A device using materials that could harness the energy from the sun and drive the electrolysis of water is a possible solution that would aid in the problem of using of fossil fuels to supply the initial electricity to split water.

#### *Basics of Semiconductors<sup>1-9</sup>*

The photoelectrochemical cell produces hydrogen similar to the process of an electrolyzer but uses semiconductors to harness the energy from the sun to drive the electrolysis of water. The semiconductor can be an n-type or p-type material. Semiconductor electrodes when placed into an electrolyte solution have been observed to generate large photocurrents relative metal electrodes. It is the photogeneration of electron/hole ( $\text{e}^-/\text{h}^+$ ) pairs within the semiconductor via band gap excitation and their charge separating ability due to the built-in electric field at the semiconductor/electrolyte junction that allow them to be candidates for water-splitting materials.

Holes are positively charged regions that are mobile and can perform chemistry. In p-type semiconductors, holes (i.e. majority carriers) are driven into the bulk and the electrons (i.e. minority carriers) are directed out to the semiconductor/electrolyte interface due to the development of an internal electric field. The strength of the field is determined by the amount of doping and other energetic features for a particular system. It is this strength that separates the electrons and holes which allows them to do work (e.g. stronger leads to better separation). For p-type materials, at the semiconductor/electrolyte interface the electrons can reduce hydrogen ions to form hydrogen gas.

For an n-type semiconductor, the majority charge carriers are electrons with the minority carriers being holes. When an n-type semiconductor is placed into an electrolyte, the holes are driven by the electric field to the surface of the semiconductor which can cause the oxidation of water to form oxygen gas and the electrons are driven into the bulk (See Figure 1).

Lastly, in order for water splitting to occur, three requirements must be met. First, the conduction and valence band edges of the semiconductor must overlap the energy levels of the hydrogen and oxygen reduction reactions. Second, the transfer of electrons or holes from the surface of the semiconductor must be fast enough to prevent corrosion and reduce energy losses. Third, the semiconductor must be stable in aqueous electrolyte and also under illumination.

## **The Experiment**

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### **Deposition**

#### *The Template*

Before making the metal salt solutions, a template of how the combinations will be organized on the fluorine doped tin oxide (FTO) conductive glass substrate should be made. It is important to decide between premixing the solutions before depositing or layering the solutions by heating between applications. Spots deposited on the FTO glass should contain approximately 10  $\mu\text{L}$  of solution and be applied to match the arrangement of the 8x8 Light Emitting Diode (LED) array. A template is provided on the SEAL website.

To premixing the solutions, it is useful to use 24 or 96 well non-treated microplates. The microplates serve as reservoirs for the solutions pre-deposition and can be made to match locations on the FTO substrate as a way to self-check the template being used. Once the combinations are created in the well-plates, ~10 mL of solution is transferred to the conductive glass via pipet. Combinations are then placed on a hot plate and heated at ~100°C to evaporate the solvent prior to placing the glass substrate in the furnace.

Layering the solutions in specific spots on the conductive glass is another method which can also be used. To accomplishing layering, one metal is deposited at a time to a given spot and is then heated to remove the solvent. Once the spot has dried, the next metal is added to the top of the spot and is again heated to remove the solvent. The amounts of each metal can be varied to create unique mixed metal combinations. This process can be repeated as many times as necessary or desired. This method is useful to examine the impact on the order of deposition of the combinations. Either method is acceptable, but different results may be observed. After deposition, samples are then fired at a minimum of 500 °C for at least 2 hours.

Typical samples will have combinations in binary, tertiary, or quaternary ratios. Initially, the metal precursors are deposited in a spot containing no other precursors, and then in 1:1 ratios with other precursors. They can then be varied to 1:2 or 2:1 ratios. As shown, many combinations start to develop with the addition of metal precursors but how and in what ratios the samples are deposited are entirely at the researcher's discretion. When manipulating molar ratios, it is easiest to keep concentrations constant. The standard concentration used in experiments is 0.04 M, but experiments have been completed with concentrations as high as 0.5 M solutions. When depositing the samples onto the FTO glass substrate,

make sure to leave portions blank. This is important to ensure that the data is correctly being recorded and no signal is observed where there is no sample.

In addition to the blank control, the standards should also be included on every plate. The standards used are an iron salt precursor solution (e.g. 0.04 M Iron (III) nitrate) which is decomposed into iron oxide to test for photoanode materials and a copper salt precursor solution (e.g. 0.04 M Copper (II) nitrate) which is decomposed into CuO to test for photocathode materials.  $\alpha\text{-Fe}_2\text{O}_3$  has shown to be a consistent n-type material that produces a photocurrent under a positive applied bias while CuO has been shown to be a consistent p-type material that produces a photocurrent under negative applied bias.

A section or at a minimum a few spots should be reserved on each glass substrate for each of the individual standards. If a signal is above that generated for copper or iron oxide, it is considered a “hit” and this warrants further investigation. Finally, a section of the FTO plate should be reserved for contact attachment (see *Contact Attachment* for further information).

Additional information on template design and spot placement is available on the Solar Energy Activity Laboratory and the SHARK website.<sup>10</sup> The sample spotting template is designed for the pipet deposition method (see *Deposition: Pipet*) and is designed to align the spots with the 8x8 LED array of the SEAL system. The printing templates are available for the SHARK system on the SHARK website. Tertiary and binary printing gradients are available for examples. The template designs should be used only for reference because students should be encouraged to develop their own ratios.

### ***Solution Prep***

Make sure to check solubility and compatibility before making solutions. In addition, all Material and Safety Data Sheets should be read prior to starting the laboratory exercise. Appropriate personal protective equipment should be worn at all times.

Precursor solutions are made using metal salts such as nitrates, chlorides, or acetates. The solutions are typically aqueous, but can be made with organic solvents such as ethanol. For spray deposition, a 50/50 mixture of water and ethanol is used to form an even thin film. (See *Deposition, Spray* for more details)

### ***Glass Substrate Cleaning***

Before deposition, FTO glass substrates can be cleaned with a diluted soap and rinsed with distilled water. After rinsing with distilled water, methanol or ethanol can then be used to make the plate slightly hydrophobic. Once the plate is dry, check to see which side is conductive by using a voltmeter.

## **Methods for Deposition**

### ***Pipet***

The sample spotting template is designed for the pipet deposition method and matches the 8x8 LED array. Once ratios are decided and solutions are made, place a cleaned glass plate on top of the printed sample spotting template. (*Note: keep setup close to hotplate for easy transferring*) Deposit a total of 10  $\mu\text{L}$  onto the conductive side of the glass plate. Metal salt solutions can be deposited with micropipettes or Hamilton syringes. If using Hamilton syringes, incorporate a rinse stage between metal salt solutions. Once all the precursor solutions are deposited according to the pre-determined ratios, carefully transfer the glass plate to a cool hot plate. Turn hotplate on to approximately 100°C and keep on until solutions have adhered to glass substrate and the solvent has been evaporated. Turn off hotplate and let cool. Once plate has cooled, transfer to furnace or kiln for sintering.

### ***Spray***

The precursor solutions can also be deposited via spray deposition using inexpensive airbrushes or glass atomizers. An inert gas such as compressed nitrogen can be used to power the airbrush which

deposits the precursor solutions. Other inexpensive spray applications can be investigated such as spray bottles and pressured bottles. When using spray deposition, the angle of the hotplate is crucial. From in-house experiments it was shown that at approximately a 45° angle, the dispensed solutions do not pool or drip before evaporation can occur. The glass substrates must be securely mounted on a hot plate with conducting side facing outward and heated at 300°C. The templates consist of aluminum metal masks with varying cut-out portions, which are mounted on the hotplate over the glass substrate to allow only small areas of the glass to be exposed at a time. The sample is then applied using quick passes of the sprayer, approximately three inches away from the glass substrate. Concentrations of the precursor solutions are generally in the 0.25-0.35 M range. The application technique may need to be adjusted to achieve the desired thickness and coverage depending on the precursor being deposited. Typically, thin films are desired because previous studies have shown that thicker films tend to exhibit decreased photocurrent.<sup>4,6</sup>

## **Formation of Mixed Metal Oxide Combinations**

After the solutions are dried on the glass substrate and cooled, they are placed in a kiln or furnace. For thermal oxidation to occur, the metals need to be exposed 200-1000°C. The varying temperature and duration changes the nanocrystalline structure of the formed metal oxide.<sup>1</sup> The suggested time and temperature is 500°C for two hours. The threshold of the FTO glass is approximately 560°C. At this point, visible deformation of the surface is present in addition to increased resistance values across the plate. After firing, allow conductive glass substrates to cool to room temperature before removing from furnace or kiln. Once cool, attach contact to conductive side of glass which is described in the next section.

## **Analysis of Combinations**

### ***Contact Attachment***

A contact must be attached to the glass substrate for connection of the working electrode lead from the data acquisition box to sample plate. The contact can either be a thin piece of graphite tape or metal wire adhered with silver epoxy. For graphite tape, attach the adhesive side of the tape to the conductive side of the glass substrate. Cover the graphite tape with electrical tape or clear epoxy to form a waterproof seal. For metal wire, attach wire with silver epoxy. Once silver epoxy is cured, cover with a coat of clear epoxy to keep the electrolyte out. Check attachments to make sure there is good electrical contact between graphite (or wire) and glass before moving on to next step.

### ***Photocurrent Measurements***

Set up kit according to instructions supplied on SEAL website. Once the kit is set up, make 1 L of ~ 0.1 M NaOH or KOH for use as the electrolyte. On top of the LED array, place a large crystallization dish containing the sample plate (working electrode) with conducting side up. Place graphite rod (counter electrode) on side of crystallization dish and secure with electrical tape. While wearing gloves, carefully fill crystallization dish with electrolyte until the sample plate is completely covered. Connect counter electrode lead from data acquisition box to graphite rod. Be careful not to have the alligator clip touch the electrolyte solution or each other. Check to make sure voltmeter to the DVM connector is set to read DC voltages and do not connect working electrode to the data acquisition box until software is opened on the computer.

Turn on data acquisition box and open software program SolarMaterialsDiscovery on computer (software can be downloaded from website). After prompt initial start up messages, a message asking for you to enter the voltage from voltmeter will appear. Do not enter the voltage. First, connect working

electrode lead from data acquisition box to graphite tape or wire connected to sample plate. Once plate is connected, line up the deposited spots with LED lights and tape the working electrode lead to side of crystallization dish so that it is immobile. Be careful not to have the alligator clip touch the electrolyte solution. Now, enter the voltage reading supplied by the voltmeter and click OK. Once you click OK, the program will start an initialization step that tests each of the LED lights. After the initialization cycle, a task menu will appear.

The task menu will have a set of options to choose from. The first task should be to apply a bias if necessary. A positive or a negative bias may be applied using the software. The value chosen should be small (e.g., 0.050V to 0.100 V) and can take a while to stabilize until it is below the 0.5V reading that is desired. Next, check the dark current reading by selecting the “Check Rest Current” from the task menu. An additional menu will pop up with rest current measurements given as voltages that are proportional to the current flowing through the cell. If the values given are less than 0.5 V, a scan can be performed. If the values are above 1 V, the applied voltage should be lowered and the process should be repeated. It is recommended to not apply a bias greater than 0.5V because greater than this value there will be too much dark current flow (background noise) for the system. The system works by integrating the current that flows during the time each LED is illuminated and subtracting the dark current flow at the same time.<sup>11</sup>

Once the dark current is stabilized, you are ready to perform a scan. From the task menu, select “Perform a scan”. A command menu will appear asking how many scans to perform. Initially, perform 1 scan to test signal. If the signal is good, perform additional scan (ie 5-10), to improve the signal to noise ratio. Once the test is completed, save data to computer and upload to SEAL website.<sup>10</sup>

## References

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## Photoelectrochemical Cell

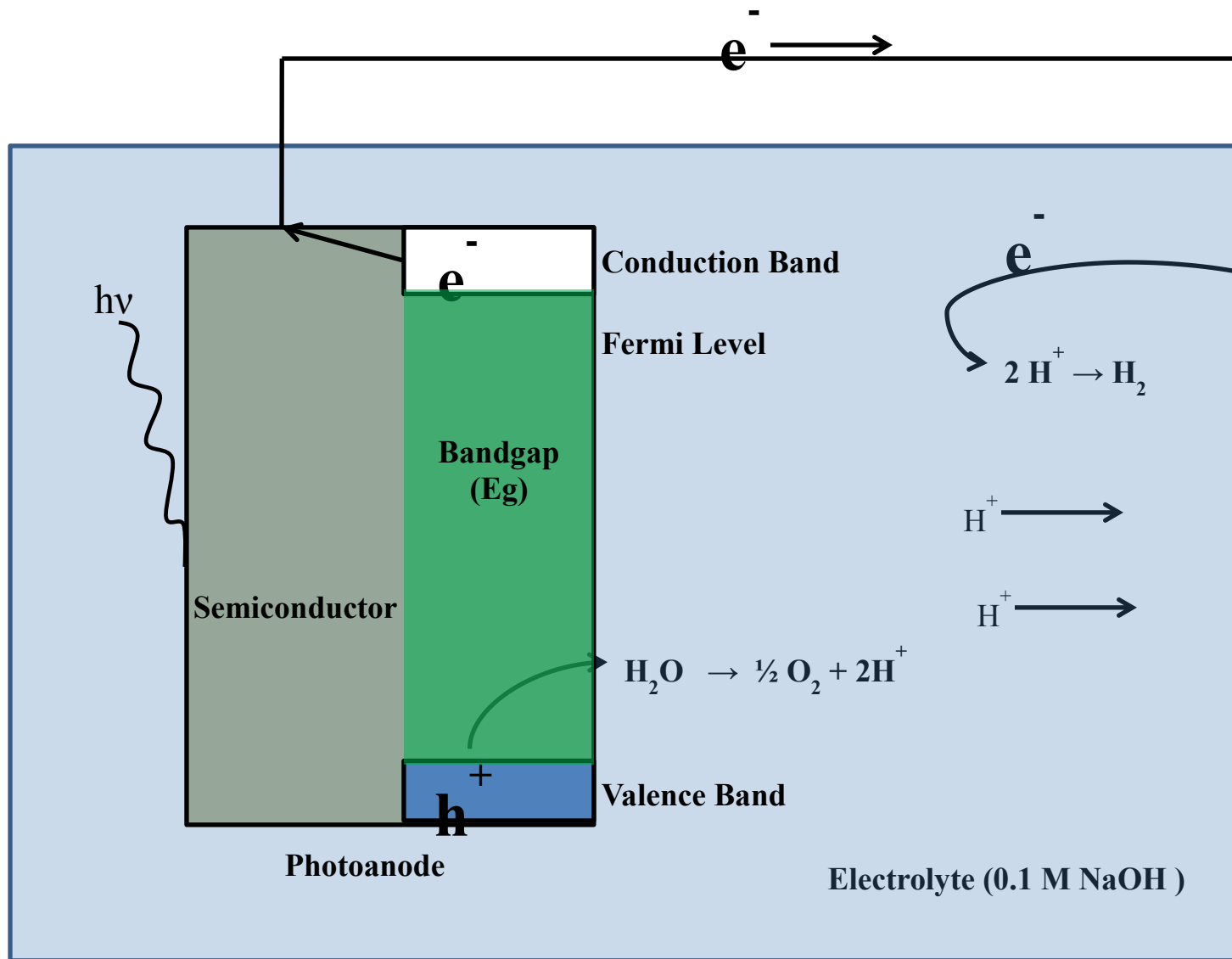


Figure 1: An example of a photoelectrochemical cell with a metal oxide semiconductor as the photoanode and a metal electrode as the cathode.

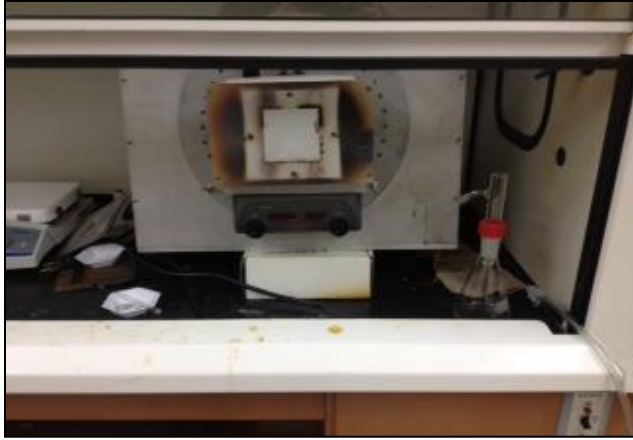


Figure 2: The spray deposition hot plate mount and glass atomizer experimental set up.